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Determination of key operating conditions for the photocatalytic treatment of olive mill wastewaters

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Abstract

The TiO₂-mediated photocatalytic treatment of olive mill wastewater (OMW) was investigated in a batch type, laboratory scale photoreactor. UV-A irradiation was provided by a 400 W, high pressure mercury lamp and Degussa P25 TiO₂ was used as the catalyst. A factorial design approach was used to study the effect of various operating conditions such as initial organic loading, TiO₂ loading, pH, contact time and the addition of hydrogen peroxide on the conversion of COD and total phenols and experimental models describing the respective removals were developed. Effluent decolorization as well as process efficiency in terms of energy consumption were also evaluated. Finally, the acute ecotoxicity of OMW samples prior to and after photocatalytic treatment was assessed.

28 *Keywords:* olive mill wastewater, TiO₂ photocatalysis, factorial design, energy consumption

29

30 1. Introduction

31 The foodstuff processing industry based on olive oil extraction is an economically important
32 activity for many regions of the Mediterranean Sea area. This process results in large quantities of
33 bio-recalcitrant effluents that come from the vegetation water and the soft tissues of the olive fruits
34 mixed with the water used at the different stages of oil production. All these wastewaters together
35 with the industry washing waters make up the so called olive mill wastewater (OMW). Essentially,
36 OMW consists of water (80–83%), organic compounds (15–18%) and inorganic compounds (2%),
37 while the organic content varies broadly depending on many parameters such as the olive variety,
38 harvesting time, climatic conditions and the oil extraction process. OMW also contains phytotoxic
39 and biotoxic substances which prevent it from being disposed of. The phytotoxicity and strong
40 antibacterial action have been attributed mainly to the polyphenolic content (0.5–24 g/L) found in
41 OMW and secondarily to fatty acids present in olive oil residues [1]. The presence of these
42 recalcitrant organic compounds constitutes one of the major obstacles in the detoxification of
43 OMW.

44 Management of OMW and alike agro-industrial effluents is a complicated and pretty much
45 unresolved issue with serious socio-economic implications. Given the unique characteristics of
46 OMW (i.e. organic content of tens of g/L COD, seasonal and localized production involving small
47 to medium size ventures), it is likely that a sequence of processes rather than a single operation may
48 become the optimum treatment option. Such scheme could benefit from the integration of low-cost
49 technologies (i.e. sedimentation, filtration, coagulation), conventional biological processes (i.e.
50 aerobic and anaerobic) and the more costly advanced chemical oxidation to meet environmental
51 regulations for discharge [2]. In recent years, advanced oxidation processes (AOPs) have been
52 employed as alternative pretreatment methods aiming at reducing organic load and bio-recalcitrance
53 of these effluents. Among them, photocatalytic methods have attracted a great deal of attention
54 regarding OMW treatment. In a recent study, El Hajjouji et al. [3] studied the UV/TiO₂ treatment of
55 OMW and found that oxidation for 24 h at 415 W intensity led to 94% phenols and 22% COD

removal respectively, while decolorization was 57%. Moreover, it was suggested that the compounds responsible for the persistent effluent COD after UV/TiO₂ attack were mainly pectins. In another recent study [4], the effect of various operating factors was investigated for the UV/H₂O₂/TiO₂ treatment of a synthetic solution containing 13 organic compounds typically found in OMW. OMW has also been treated by UV irradiation combined with other techniques such as ultrafiltration and ozonation [5, 6]. Reports on solar photocatalytic and photo-Fenton processes have also been published [7-9]. The possibility of reducing OMW phytotoxicity by means of solar irradiation combined with the Fenton reagent was investigated by Andreozzi et al. [7] and it was found that this process was not so efficient compared to other AOPs such as ozonation. On the other hand, the photo-Fenton process successfully removed 85% COD and up to 100% of phenolic compounds at a pilot-plant solar photoreactor [8].

The aim of this work was to study the photocatalytic oxidation of OMW regarding the effect of various operating conditions such as TiO₂ loading, initial organic loading, initial pH, contact time and the addition of hydrogen peroxide on the conversion of COD and total phenols (TPh). These parameters were chosen as they typically play a key role in dictating the performance of photocatalytic reactions. A factorial design methodology was adopted to determine in a systematic way the statistical significance of each parameter. Energy consumption of the process and ecotoxicity of OMW samples prior to and after treatment were also investigated.

74

2. Experimental and analytical

2.1. Materials

The OMW was provided by a three-phase olive oil mill company, located in Chania, Western Crete, Greece. The effluent was subjected to filtration to remove most of its total solids. The effluent has a strong olive oil smell and a dark black-brown color with maximum absorbance in the visible region at $\lambda=550$ nm. Its main properties prior to and after filtration are given in Table 1.

81 Degussa P25 TiO₂ was kindly supplied by Degussa AG (anatase:rutile 75:25, 21 nm primary
82 crystallite particle size, 50 m²/g BET surface area) and it was used as received. Hydrogen peroxide,
83 as a 35% w/w solution, was supplied by Fluka.

84

85 2.2. Photocatalytic Experiments

86 UV-A irradiation was provided by a 400 W high pressure mercury lamp (Osram, HQL, MBF-U).
87 The emission spectrum of the lamp consists of several spectral lines in the UV and visible region of
88 which the main emission line exists at 366 nm [10]. Emission below 300 nm is impeded due to the
89 reactor's material of construction (borosilicate glass). The photon flux emitted from the lamp was
90 determined actinometrically using the potassium ferrioxalate method and was found to be $1.12 \cdot 10^{-5}$
91 einstein/s.

92 Experiments were conducted in an immersion well, batch type, laboratory scale photoreactor
93 described in detail elsewhere [11]. In a typical photocatalytic run, the original OMW was diluted
94 with distilled water to achieve the desirable initial organic loading. Afterwards, 350 mL of the
95 effluent were loaded in the reaction vessel and the solution was slurried with the appropriate
96 amount of TiO₂. The resulting TiO₂ suspension was magnetically stirred for 30 min in the dark to
97 ensure complete equilibration of adsorption/desorption of OMW organic compounds onto the
98 catalyst surface which was about 10% in terms of COD. After that period of time, the lamp was
99 turned on (this was taken as "time zero" for the reaction), while air was continuously sparged in the
100 liquid and the reaction mixture was continuously stirred. Regarding the initial pH that took values
101 of 4.8 (natural pH of the diluted effluent) and 7 (after adjustment with a few drops of 1 M NaOH
102 solution), it should be noticed that the solution was not buffered to the aforementioned values.
103 However, pH was monitored constantly throughout the reaction showing that only marginal
104 changes had occurred between the initial and final solutions. In those cases where experiments were
105 performed in the presence of hydrogen peroxide, the appropriate amount of 35% w/w solution of
106 H₂O₂ was added to achieve the desirable final concentration of H₂O₂. All experiments were

107 conducted at constant temperature of $28\pm 2^{\circ}\text{C}$. For each experimental run, 3 samples were taken, i.e.
108 the first at the beginning of the experiment (time zero), the second after 1 hour of treatment and the
109 third after 4 hours of treatment. The samples were filtered to remove solid particles and then
110 analyzed for their residual COD, total phenolic content (TPh) and color.

111

112 *Analytical measurements*

113 COD was determined by the dichromate method. The appropriate amount of sample was introduced
114 into commercially available digestion solution (0-1500 mg/L) containing potassium dichromate,
115 sulfuric acid and mercuric sulfate (Hach Europe, Belgium) and the mixture was then incubated for
116 120 min at 150°C in a COD reactor (Model 45600-Hach Company, USA). COD concentration was
117 measured colorimetrically using a DR/2010 spectrophotometer (Hach Company, USA).

118 The total phenolic content was determined colorimetrically at 765 nm on a Shimadzu UV 1240
119 spectrophotometer using the Folin-Ciocalteu reagent according to the procedures described in
120 detail elsewhere [12]. Gallic acid monohydrate was used as standard to quantify the concentration
121 of total phenols in OMW.

122 Sample absorbance was scanned in the 400-800 nm wavelength region on a Shimadzu UV 1240
123 spectrophotometer. Color was measured at $\lambda=550$ nm, which corresponds to the maximum
124 absorbance in the visible region. Changes in sample absorbance at the wavelength of 550 nm were
125 monitored to assess the extent of decolorization that had occurred during photocatalytic treatment.

126 H_2O_2 concentration in the OMW solution was monitored using Merck peroxide test strips (0-25 mg
127 $\text{H}_2\text{O}_2/\text{L}$ and 0-100 mg $\text{H}_2\text{O}_2/\text{L}$), while the pH was measured by a Toledo 225 pH meter during
128 photocatalytic treatment.

129 The luminescent marine bacteria *V. fischeri* was used to assess the acute ecotoxicity of OMW
130 samples. The inhibition of bioluminescence of *V. fischeri* was measured using a LUMISTox analyzer
131 (Dr. Lange, Germany). Toxicity is expressed as EC_{50} , which is the effective concentration of a
132 toxicant causing 50% reduction of light output during the designated time intervals at 15°C .

133

134 **3. Results and discussion**

135 *3.1. Effect of operating parameters*

136 In this work, a statistical approach was chosen based on a factorial experimental design that would
137 allow us to infer about the effect of the variables with a relatively small number of experiments
138 [13]. Five independent variables that may affect the photocatalytic treatment of OMW were taken
139 into account, namely initial COD concentration, TiO₂ loading, solution pH, treatment time and
140 H₂O₂ concentration. The experimental design followed in this work was a full 2⁵ experimental set,
141 which required 32 experiments. The order each experiment was performed was selected randomly.
142 The design matrix of the experiments and the statistical analysis of these were made by means of
143 the software package Minitab 14. The values chosen for the independent variables and the results
144 obtained in terms of two measured response factors (dependent variables), namely concentration of
145 COD oxidized in mg/L (response factor Y₁) and concentration of TPh removed in mg/L (response
146 factor Y₂) are presented in Table 2. Table 2 also shows percent removal of COD, TPh and color.
147 Statistical treatment of the response factors Y₁ and Y₂ according to the factorial design technique
148 involves the estimation of the average effect, the main effects of each individual variable as well as
149 their two and higher order interaction effect [13]. The average effect is the mean value of each
150 response factor, while the main and interaction effects are the difference between two averages:
151 main effect = $\bar{Y}_+ - \bar{Y}_-$, where \bar{Y}_+ and \bar{Y}_- are the average response factors at the high and low level
152 respectively of the independent variables or their interactions. Estimation of the average effect, as
153 well as the main and interaction effects was made by means of the statistical package Minitab 14
154 and the results are summarized in Table 3.

155 A key element in the factorial design statistical procedure is the determination of the significance of
156 the estimated effects. For the assessment of the significance of the main and interaction effects in
157 un-replicated factorial designs, Minitab uses the Lenth's pseudo-standard error (PSE) [13, 14].
158 Lenth's PSE is an estimate of the standard error of the effects and for its calculation the median, m,

159 of the absolute values of the effects is first determined and then $PSE=1.5 \times m$. Any estimated effect
160 exceeding $2.5 \times PSE$ is excluded and, if needed, m and PSE are recalculated. Then, a margin of
161 error (ME) is given by $ME= t \times PSE$, where t is the $(1 - \alpha/2)$ quantile of a t-distribution with
162 degrees of freedom equal to the number of effects/3 [13, 14]. The present study was done for a
163 confidence interval of 95%, therefore $\alpha=0.05$. The calculated values of PSE and ME for the two
164 response factors according to the Minitab software are also given in Table 3. All estimated effects
165 greater than the ME can be considered significant. On the other hand, all other effects whose values
166 are lower than the ME can be attributed to random statistical error.

167 A very useful pictorial presentation of the estimated effects and their statistical importance can be
168 accomplished using the Pareto chart of the effects. The Pareto chart displays the absolute values of
169 the effects in the ordinate, while a reference line is drawn at the margin of error, and any effect
170 exceeding this reference line is potentially important. The Pareto charts of the effects for the COD
171 and TPh oxidation are shown in Figs. 1 and 2 respectively.

172 As can be seen in Fig. 1, there are basically only two effects which are statistically important for
173 COD oxidation, namely, in decreasing order of significance: the reaction time, and the initial
174 concentration (influent) of COD. These effects are the most important factors affecting the
175 oxidation of COD. The presence of oxidant, TiO_2 loading and the initial solution pH, along with all
176 interactions, are not significant and may be explained as random noise. Both significant effects are
177 positive indicating that an increase in their level brings about an increase in the amount of COD
178 oxidized. The slightly positive (but still insignificant) effect of hydrogen peroxide on degradation
179 may be due to the low H_2O_2 :COD concentration ratio employed in this work, i.e. the additional
180 oxidizing species generated by the dissociation of H_2O_2 lead to a measurable but marginal
181 enhancement of degradation. In photocatalytic reactions, conversion invariably increases with
182 increasing TiO_2 concentration up to a point above which it levels off; this corresponds to the point
183 where all catalyst particles are fully illuminated. At higher concentrations, a screening effect of
184 excess particles occurs, thus hindering light penetration; this usually results in conversion reaching

185 a plateau, while at excessive catalyst concentrations conversion may also decrease due to increased
 186 light reflectance [4, 11]. It appears that the catalyst concentrations employed in this work fall within
 187 this range, thus having a slightly negative but not statistically important influence on COD
 188 conversion. A change in initial pH from 4.8 to 7 has no effect on conversion and this is consistent
 189 with the results of Silva *et al* [4] who found that the photocatalytic treatment of a synthetic OMW in
 190 the pH range 3.5-8 gave almost identical final conversions. It should be noticed here that the point
 191 of zero charge of Degussa P25 TiO₂ is at pH=6.8; for the range of pH values in question, the
 192 catalyst ionization state would remain unchanged (e.g. positively charged) and consequently would
 193 not affect the degree of adsorption/reaction onto the surface.

194 Based on the variables which are statistically significant, a model describing the experimental
 195 response Y₁ was constructed:

196

$$197 \quad Y_1 = 601.75 + 184.5X_4 + 92X_1 \quad (1)$$

198

199 where Y₁ is the mass of COD oxidized (mg/L), X_i are the transformed forms of the independent
 200 variables according to:

$$201 \quad X_i = \frac{Z_i - \left(\frac{Z_{high} + Z_{low}}{2} \right)}{\left(\frac{Z_{high} - Z_{low}}{2} \right)} \quad (2)$$

202 and Z_i are the original (untransformed) values of the variables. The coefficients that appear in
 203 equation (2) are half the calculated effects, since a change of X=-1 to X=1 is a change of two units
 204 along the X axis.

205 The model predicts a linear dependency of the mass of COD oxidized on the operating variables.
 206 Not only this, but it also indicates that the contact time (x₄) is the most significant variable in terms
 207 of COD removal, because its effect has the highest value and its about two times greater than the
 208 effect of influent organic loading (x₁). Therefore, the factorial design analysis shows that

209 photocatalytic treatment is more efficient, in terms of mass of pollutants removed, at increased
210 organic loadings, thus implying that the concept of severe OMW dilution (usually with other
211 industrial [15] or municipal wastewaters [16]) prior to treatment may be revisited. This undoubtedly
212 enhances the use of TiO₂-mediated photocatalysis for OMW treatment.

213 Regarding TPh removal, the Pareto chart of the effects (Fig. 2) shows that contact time, influent
214 COD and their interaction have a significant positive effect. On the other hand, the interactions of
215 initial COD, TiO₂ and H₂O₂ loading as well as the interaction between TiO₂ loading and initial
216 H₂O₂ concentration have a significant negative effect on TPh removal.

217 The following experimental model describes the TPh removal in mg/L:

218

$$219 \quad Y_2 = 113.53 + 34.16X_4 + 30.91X_1 - 22.34X_1X_2X_5 - 18.97X_2X_5 + 15.91X_1X_4 \quad (3)$$

220

221 It can be observed from eqn 3 that, contrary to eqn 1, the effect of the contact time is not much
222 greater than the effect of the influent COD. Moreover, the effect of TiO₂ loading has an indirect
223 negative effect on TPh removal through its interaction with initial COD and H₂O₂ concentrations.

224 On the assumption that TPh are represented by gallic acid monohydrate, the stoichiometry of its
225 reaction to carbon dioxide and water dictates that 100 mg of gallic acid would require 102 mg
226 oxygen for the complete oxidation; therefore, Y₂ in Table 2 practically corresponds to the
227 concentration of COD oxidized due to the phenolic fraction of the effluent. Comparison between Y₁
228 and Y₂ clearly shows that TiO₂ photocatalysis is a non-selective oxidation process, attacking
229 simultaneously TPh and other organics.

230 In terms of color removal, decolorization mainly takes place during the first hour of treatment under
231 almost all experimental conditions. As seen in Table 2, decolorization is always greater than 80%,
232 and in most cases it is over 95%, at low influent COD; conversely, for influent COD of 5100 mg/L
233 color removal typically varies between 40 and 70%. Interestingly, complete decolorization

coincides with equally high levels of TPh removal, thus implying that the OMW dark color is mainly due to the presence of phenolic compounds and their polymerized derivatives.

The validation of the mathematical model was based on the calculation of the residuals, which are the observed minus the predicted values according to the model, for the two response factors. The values of the calculated residuals for the two response factors were plotted in a normal probability plot and the results are shown in Figs. 3 and 4. For both responses, almost all data points lie close to a straight line and within the 95% confidence interval lines. These results indicate that the calculated residuals follow a normal distribution with mean values near zero. According to the above observations, it can be concluded that there is a good agreement between the experimental values and the mathematical model developed and the observed differences (i.e. the residuals) may be readily explained as random noise.

Eventually, the development of empirical mathematical models with relatively few experiments to describe OMW mineralization and TPh degradation is of great importance. Based on these models, an indicative view for scaling-up the process can be obtained.

Energy consumption

AOPs based on artificial light may be associated with increased operating costs, a major fraction of which is related to energy consumption. Bolton *et al* [17] introduced the concept of specific electric energy consumption per unit mass of pollutant (e.g. COD) degraded (E_{EM}):

$$E_{EM} = \frac{Pt}{V(COD_0 - COD)} \quad (4)$$

where V is the effluent volume in liters, t is the treatment time in hours, P is the lamp power in kW, COD_0 and COD is the concentration in g/L before treatment and after time t respectively. Eqn (4) assumes that the reaction is zero-order with respect to COD, i.e. the removal rate is directly proportional to the rate of electric energy consumption. Although a thorough kinetic analysis was

outside the scope of this work, an attempt was made to evaluate the apparent order of reaction with respect to COD concentration based on the experimental data of Table 2. If the reaction were first-order, COD conversion would remain constant for runs performed at different initial COD values and all other variables being identical; conversely, for zero-order kinetics an increase in initial COD would result in a similar conversion decrease. In most cases (e.g. see runs 1 and 11, 2 and 12, 5 and 20, 6 and 22, 7 and 14, 9 and 19, 15 and 23, 26 and 32, 28 and 31), a 5-fold COD increase (i.e. from 1000 to 5100 mg/L) yields a decrease in the conversion by about 4-5 times, thus implying that the apparent reaction rate is near zero-order.

Applying eqn (4), it is evident that photocatalytic treatment is more efficient, in terms of energy consumption, at high influent COD values and short treatment times. For instance, comparing runs 29 and 17 energy consumption is 4.5 and 1.8 kWh/g COD removed after 1 h at 1000 and 5100 mg/L influent COD respectively; these values become 11 and 5 kWh/g COD removed after 4 h of treatment (runs 13 and 18). This fact comes to boost the conclusion, drawn from the factorial design analysis, that photocatalytic treatment is more efficient when working at increased organic loadings. Similar arguments can be inferred for TPh removal; energy consumption is 26.5 and 9 kW/g TPh removed after 1 h and 61 and 14.2 kW/g TPh removed after 4 h at 1000 and 5100 mg/L influent COD respectively (applying again eqn (4)). These values are seemingly greater than those for COD as the phenolic content comprises only a fraction of the total organic content.

278

279 *Acute toxicity*

The untreated effluent was highly ecotoxic to *V. fischeri* with an EC_{50} value of 12%. Changes in ecotoxicity were found to depend strongly on the residual organic matter following treatment. For instance at the conditions of run 23, the resulting effluent with a residual organic content of about 200 mg/L COD was non-toxic and this can be attributed to the complete removal of TPh. Conversely, when the experiment was performed at increased influent COD (run 15), the

285 ecotoxicity of the treated effluent remained nearly unchanged ($EC_{50}=15\%$), thus indicating that the
286 residual 4150 mg/L COD (including about 200 mg/L TPh) contain various toxic species.

287

288 **4. Closing remarks**

289 Diluted wastewater from the olive oil industry was treated by TiO_2 photocatalysis with emphasis
290 given on the effect of various operating conditions on treatment efficiency with regard to COD and
291 TPh removal as well as decolorization. In order to evaluate the importance of the various
292 parameters involved in a coherent way, a factorial design methodology was followed. The
293 conclusions drawn from this study can be summarized as follows:

294

295 (1) COD removal was positively affected mostly by contact time and secondly by influent COD. All
296 other variables had no significant statistical importance to COD removal response. TPh removal
297 was positively affected by contact time and influent COD, while there was a negative effect through
298 the interaction of influent COD, TiO_2 and H_2O_2 concentrations.

299 (2) Simple, empirical models were developed and adequately simulated quantitatively the amount
300 of COD and TPh removed as a function of the most statistically significant effects for the range of
301 operating variables in question. These models may provide a useful tool for scaling-up and making
302 an economic analysis for an industrial application of the proposed process.

303 (3) Energy consumption per unit mass of pollutant removed is lower for high influent COD,
304 indicating that TiO_2 photocatalysis can be a promising process for OMW treatment.

305 (4) Monitoring ecotoxicity during photocatalytic treatment showed that OMW was almost
306 completely detoxified at low influent COD, while toxicity was only slightly reduced at increased
307 organic loadings.

308

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314

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- 343

344 **Table 1.** Properties of OMW samples used in this study.

Properties	Before filtration	After filtration
COD, g/L	47	40
Total phenols (TPh), g/L	8.1	3.5
Total solids, g/L	50.3	0.6
TOC, g/L	16.9	14
pH	4.6	4.4
Conductivity, mS/cm	17	18

345

346

347 **Table 2.** Design matrix of the 2⁵ factorial experimental design and observed response factors (Y₁:
348 mg of COD removed per liter; Y₂: mg of TPh removed per liter) as well as percent removal of
349 COD, TPh and color.

Run order	X ₁ , [COD] ₀ , mg/L	X ₂ [TiO ₂], g/L	X ₃ pH	X ₄ Reaction time, h	X ₅ [H ₂ O ₂], mg/L	Y ₁ COD oxidized, mg/L	Y ₂ TPh oxidized, mg/L	% COD removal	% TPh removal	% Color removal
1	1000	2	7	1	500	286	72	29	77	95
2	1000	2	7	4	500	906	102	92	99	99
3	5100	0.5	7	1	0	790	49	15	11	9
4	1000	0.5	4.8	1	500	382	67	37	73	89
5	5100	0.5	7	1	500	400	144	8	27	38
6	5100	2	4.8	4	500	950	73	18	20	61
7	5100	0.5	7	4	0	860	155	17	34	28
8	5100	2	4.8	1	500	730	78	15	22	46
9	5100	2	7	1	0	370	66	7	12	18
10	5100	0.5	7	4	500	550	282	11	53	50
11	5100	2	7	1	500	390	78	8	19	63
12	5100	2	7	4	500	810	169	17	42	74
13	1000	2	4.8	4	0	412	75	42	85	93
14	1000	0.5	7	4	0	758	101	74	99	95
15	5100	0.5	4.8	4	500	950	205	19	43	58
16	1000	0.5	7	1	0	256	57	25	61	77
17	5100	2	4.8	1	0	630	125	12	24	39
18	5100	2	4.8	4	0	970	322	18	63	66
19	1000	2	7	1	0	254	67	25	55	76
20	1000	0.5	7	1	500	288	67	32	73	96
21	1000	0.5	7	4	500	820	109	91	99	99
22	1000	2	4.8	4	500	752	101	81	99	94
23	1000	0.5	4.8	4	500	798	104	78	99	93
24	1000	0.5	4.8	1	0	78	72	7	60	70
25	1000	2	4.8	1	500	360	70	39	71	82
26	1000	0.5	4.8	4	0	918	113	92	95	96
27	5100	0.5	4.8	1	500	660	126	13	27	47
28	5100	2	7	4	0	570	216	11	41	43
29	1000	2	4.8	1	0	252	43	26	49	64
30	5100	0.5	4.8	1	0	550	89	11	18	45
31	1000	2	7	4	0	636	102	62	85	97
32	5100	0.5	4.8	4	0	920	134	18	27	52

350

351

352 **Table 3.** Average and main effects of the independent variables and their two and higher order
 353 interactions of the 2^5 factorial design on the response factors Y_1 and Y_2 .

Effect	Value of Effect	
	COD removal	TPh removal
<i>Average Effect</i>	601.75	113.53
<i>Main Effects</i>		
x ₁	184	61.81
x ₂	-43.75	-7.19
x ₃	-85.5	2.44
x ₄	369	68.31
x ₅	50.5	3.81
<i>Two-factor Interactions</i>		
x ₁ x ₂	11.25	0.06
x ₁ x ₃	-117	-1.56
x ₁ x ₄	-111.5	31.81
x ₁ x ₅	-78	-3.94
x ₂ x ₃	-18.75	-4.31
x ₂ x ₄	-27.25	1.81
x ₂ x ₅	85.75	-37.94
x ₃ x ₄	-9.5	11.19
x ₃ x ₅	-56	22.44
x ₄ x ₅	11	-12.94
<i>Three-factor Interactions</i>		
x ₁ x ₂ x ₃	-63.75	-13.81
x ₁ x ₂ x ₄	64.75	6.31
x ₁ x ₂ x ₅	26.75	-44.69
x ₁ x ₃ x ₄	-38.00	9.94
x ₁ x ₃ x ₅	-26.50	24.44
x ₁ x ₄ x ₅	1.50	-11.44
x ₂ x ₃ x ₄	73.25	-4.81
x ₂ x ₃ x ₅	60.25	4.19
x ₂ x ₄ x ₅	60.30	-20.44
x ₃ x ₄ x ₅	60.00	8.69
<i>Four-factor Interactions</i>		
x ₁ x ₂ x ₃ x ₄	-10.75	-4.06
x ₁ x ₂ x ₃ x ₅	67.25	14.19
x ₁ x ₂ x ₄ x ₅	-47.75	-20.44
x ₁ x ₃ x ₄ x ₅	2.50	8.94
x ₂ x ₃ x ₄ x ₅	-16.75	8.69
<i>Five-factor Interactions</i>		
x ₁ x ₂ x ₃ x ₄ x ₅	39.25	9.44
Lenth's PSE	73.69	13.03
ME	163.5	28.91

356 **List of figures**

357

358 **Fig. 1.** Pareto chart of the effects for COD oxidation. White bars: positive effects; hatched bars:
359 negative effects. The dotted line is drawn at the margin of error (ME).

360 **Fig. 2.** Pareto chart of the effects for TPh oxidation. White bars: positive effects; hatched bars:
361 negative effects. The dotted line is drawn at the margin of error (ME).

362 **Fig. 3.** Normal probability plot of the residuals at 95% confidence interval for the response factor
363 Y_1 .

364 **Fig. 4.** Normal probability plot of the residuals at 95% confidence interval for the response factor
365 Y_2 .

366

367

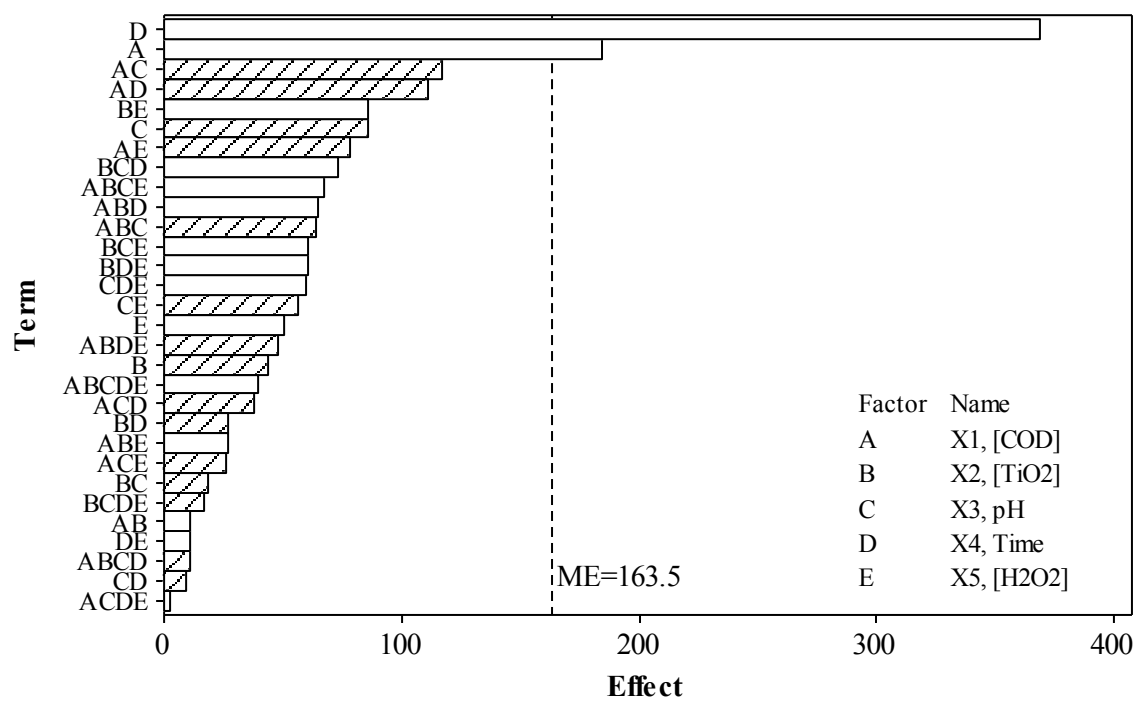


Figure 1

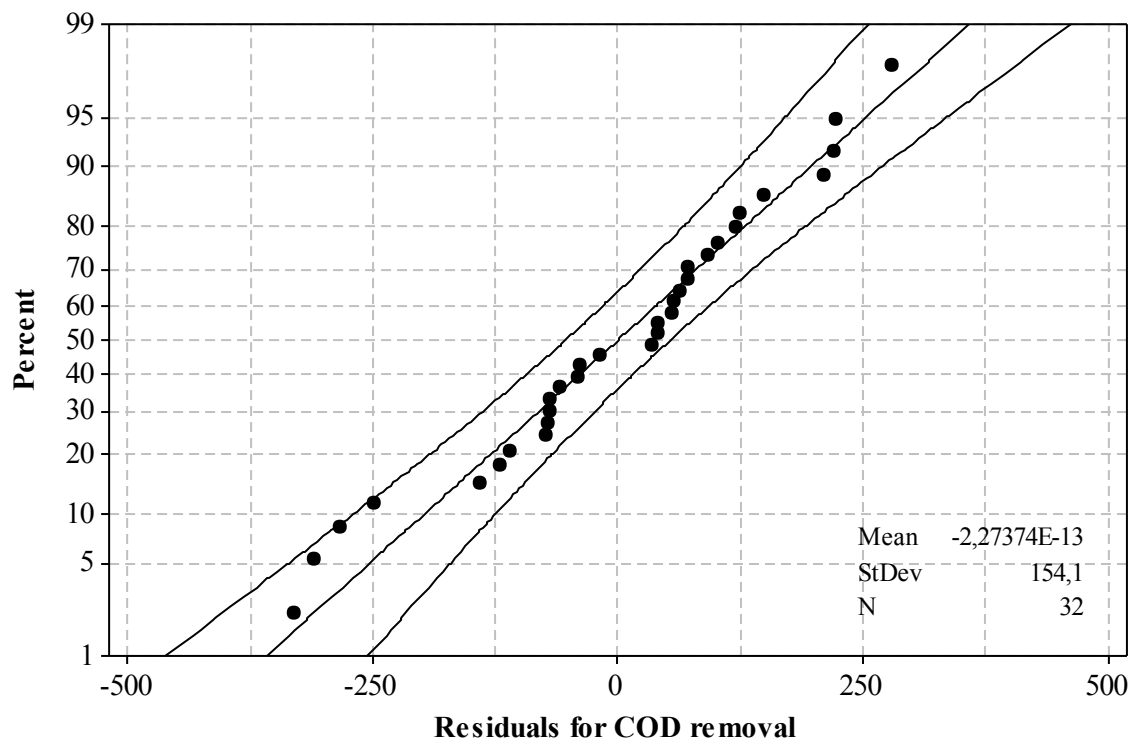


Figure 3

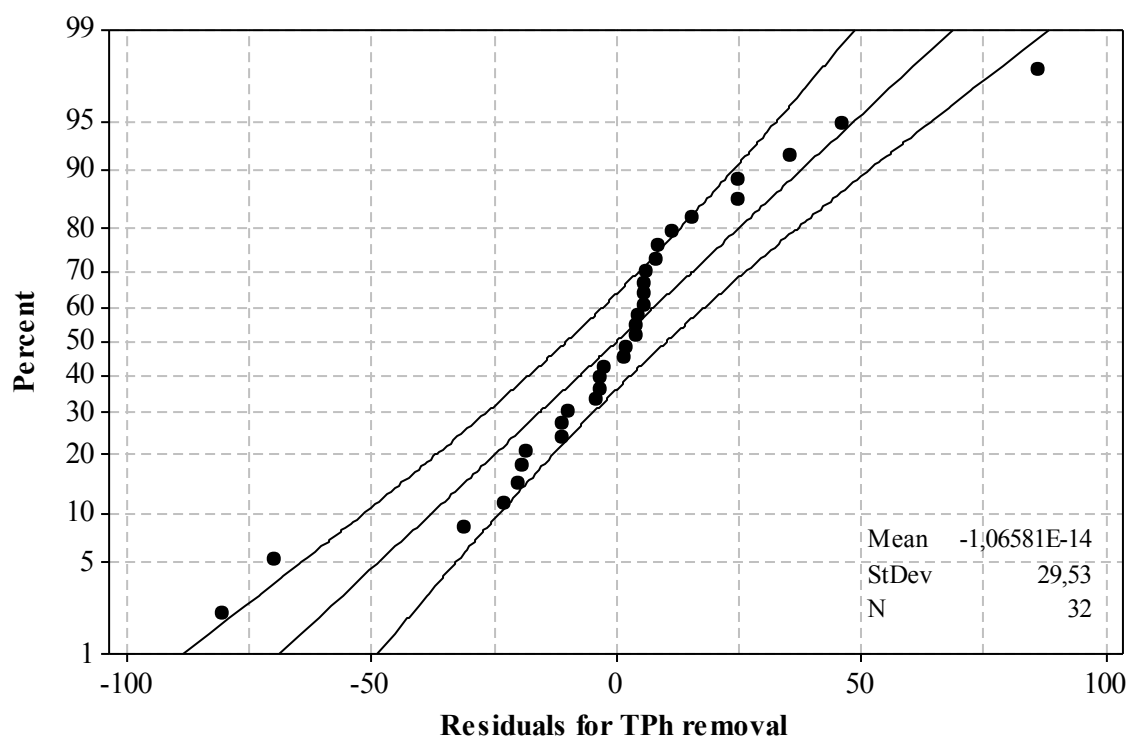


Figure 4